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Effects of Pulping Conditions on the Bleachability of Hardwood Kraft Pulps:  
1. Effects of Effective Alkali Charge in the Pulping of Birch and Maple

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# EFFECTS OF PULPING CONDITIONS ON THE BLEACHABILITY OF HARDWOOD KRAFT PULPS: 1.EFFECTS OF EFFECTIVE ALKALI CHARGE IN THE PULPING OF BIRCH AND MAPLE

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## ABSTRACT

The objective of this work was to study the effects of digester alkali charge on the chlorine dioxide bleachability of hardwood kraft pulps. We prepared birch and maple pulps with unbleached kappa numbers in the 19-20 range at two effective alkali (EA) levels, 14% and 20% ( $\text{Na}_2\text{O}$ ). These were bleached in the  $\text{D}_0(\text{EO})\text{D}_1\text{ED}_2$  sequence. A kappa factor of 0.2 was used throughout and various combinations of  $\text{ClO}_2$  charges in  $\text{D}_1$  and  $\text{D}_2$  stages were investigated. The response to  $\text{ClO}_2$  in the  $\text{D}_1$  and  $\text{D}_2$  stages was characterized in terms of the values of the parameters in a simple mathematical model, which were then subjected to statistical analysis. The result was a model that describes and predicts the effect of EA on ECF bleachability.

In the case of birch, increasing EA gave an unbleached pulp of higher brightness, lower total yield, higher rejects and lower viscosity. The high-EA maple pulp, on the other hand, had much higher brightness than its low-EA counterpart but similar yield, rejects and viscosity levels. Increasing EA substantially increased the brightness ceiling of both the hardwood species. After the  $\text{D}_1$  stage, the brightnesses of both high-EA pulps were about 5 points higher than those of their low-EA counterparts and the brightness advantage of maple over birch was maintained. It was possible to prepare pulps of 93% ISO brightness in three stages from high-EA maple pulp. After the 5-stage sequence, the high- and low- EA pulps exhibited brightness ceilings of 94% ISO and 92% ISO, respectively. The corresponding birch pulps had brightness ceilings close to 90% ISO, and brightnesses near the ceiling were reached with lower consumption of  $\text{ClO}_2$  in the case of high-EA pulp.

At moderate levels of  $\text{ClO}_2$  consumption, increasing EA allowed substantially higher brightness to be reached after three stages of bleaching in the case of maple, and after five stages in case of birch. Much of the beneficial effect of increasing EA can be attributed to an unbleached pulp brightness advantage that was retained through the bleaching sequence, except in the case of five-stage bleaching of birch with high  $\text{ClO}_2$  charges.

## INTRODUCTION

The United States Environmental Protection Agency's "Cluster Rules" place strict regulations on control and quality of effluent and air emissions (1). In order to comply with the new rules, bleached pulp mills will use increasing amounts of chlorine dioxide, implementing so-called "elemental chlorine free" (ECF) bleaching. The replacement of the cheaper chlorine with chlorine dioxide will increase the cost of production. The bleaching chemical cost can be cut back if we can develop new pulping processes or improve on the existing processes to produce pulps that are easy to bleach and consume less bleaching chemical. With this aim, we have initiated studies of the effects of individual pulping variables on the ECF bleachability of kraft pulps at constant unbleached kappa number.

In earlier work, we reported the effect of EA on ECF bleachability of southern pine over a range of kappa numbers (2). It was found that the brightness ceiling in the  $\text{D}_0(\text{EO})\text{D}_1$  sequence can be increased by increasing EA and decreasing unbleached kappa number. The effect of EA on brightness ceiling after  $\text{D}_0(\text{EO})\text{D}_1\text{ED}_2$  bleaching depends on the unbleached kappa number. At higher kappa number (~27), an increase in EA leads to an increase in brightness ceiling from 88 to 90% ISO. But EA has little effect on brightness ceiling at lower kappa number (~15). Also, at low kappa number, high-EA pulps consume more

ClO<sub>2</sub> than low-EA pulps to reach a given brightness after bleaching.

Not much work is reported in the literature on the influence of individual pulping variables on the bleachability of North American hardwood species. Recently a Canadian kraft mill reported results of high alkali pulping trials of mixed hardwood species aimed at compensating for the loss in throughput during winter months (3). They found that cooking time to achieve the same final K number was reduced by 10 minutes with a small increase in active alkali charge from 16.0 to 16.5%. No significant change was reported in dirt content, rejects, brown stock freeness or final pulp properties. Aurell (4) reported the effect of effective alkali on different wood components of birch during kraft cooking. He found that at 15% EA almost 65% of the xylan was left in pulp as compared to 50% of the xylan at 24% EA. This difference was partly attributed to a more extensive degradation and partly to a more pronounced dissolution of xylan molecules at high alkalinity. Reeve and Weishar investigated the bleaching response of three pure hardwood species in ECF bleaching sequences (5). Maple, oak and gum were bleached to a final brightness of 86% ISO by D(EO)D and D(EO)(D/N)D sequences, with and without oxygen delignification. They found that oak was more difficult to bleach than maple and gum. Hanna et al. (6) studied the effect of alkali concentration in displacement batch cooking on pulp yield, bleachability, refinability, hexeneuronic content and residual lignin structure. They found that when the total effective alkali applied was decreased substantially from 14.8 to 10.7%, aspen required a higher kappa factor and more total active chlorine to reach target brightness. However, hexeneuronic acid content did not appear to affect the bleachability of either aspen or pine.

In the work reported here, we have studied the effect of EA on ECF bleachability of kraft pulps from two North American hardwood species - birch and maple. These studies have been carried out at constant unbleached kappa number (19-20) to evaluate bleaching responses unaffected by differences in lignin content.

## EXPERIMENTAL

Birch and maple logs were kindly supplied by the Quinnesec, MI, mill of Champion International Corporation. They were chipped in a pilot scale Carthage chipper and screened. The fraction passing through a screen with 1-inch openings and retained by a ¼-inch screen was used. Pulping was carried out in an M/K Systems 6-L laboratory digester using liquors prepared from reagent grade sodium hydroxide and sodium sulfide. Pulping conditions were as follows: maximum temperature 170°C; time to maximum temperature, 90 min; liquor-to-wood ratio, 4:1; and sulfidity, 25%. All pulping chemical charges, including EA (NaOH + ½ Na<sub>2</sub>S), are expressed in terms of Na<sub>2</sub>O. Sulfidity is expressed as a percentage of active alkali (NaOH + Na<sub>2</sub>S).

After pulping, the cooked chips were disintegrated by vigorous agitation and screened on a Valley flat screen having 0.008-inch slots. The kappa number, viscosity, and brightness of each pulp were then determined prior to bleaching.

Chlorine dioxide delignification (D<sub>0</sub>)-stages were conducted in a Quantum Technologies Mark III high-shear laboratory bleaching reactor under the following conditions: kappa factor, 0.20; 30 min; 45°C; and 10% consistency. Oxygen-reinforced alkali extraction (EO) stages were conducted in a pressurized reactor equipped with a horizontal-shaft pin mixer rotating at approximately 100 rpm, under the following conditions: NaOH charge, 1.6%, o.d. pulp basis; 60 min; 70°C; and 10% consistency. The oxygen pressure was initially 60 psi and was decreased by 12 psi at 5-min intervals thereafter. Chlorine dioxide brightening stages were conducted in sealed Kapak™ bags. Dilution water and NaOH solution were added to the pulp in the bag, which was then thoroughly mixed by kneading the bag. ClO<sub>2</sub> solution was then mixed with the pulp, and the bag was sealed and placed in a temperature-regulated water bath for the required time.

Kappa number, viscosity, and brightness were determined by TAPPI test methods T236, T230, and T525, respectively. Handsheets for the brightness testing were prepared according to TAPPI test method T272.

Hexeneuronic acid (hexA) was determined in unbleached pulp by the method of Vuorinen et al. (7).

Briefly, 5.0g o.d. pulp was refluxed with 150 mls of 10 mM sodium formate solution at 100°C, 3.0% consistency for 5.0 hours. The pH of the reaction was 3.5. After the treatment the hydrozylate was analyzed by ultraviolet spectroscopy for the reaction product, 2-furoic acid.

Black liquor samples were analyzed for residual NaOH by titration to pH 11. The pH's of all the black liquor samples were also measured.

## RESULTS AND DISCUSSION

### Unbleached Pulps

To study the effect of EA on ECF bleachability at constant kappa number, it was first necessary to establish the cooking time necessary to achieve the target kappa number. A series of pulping experiments in which cooking time was varied at three EA levels, 12, 16, and 20%, gave the results as shown in Figures 1 and 2.

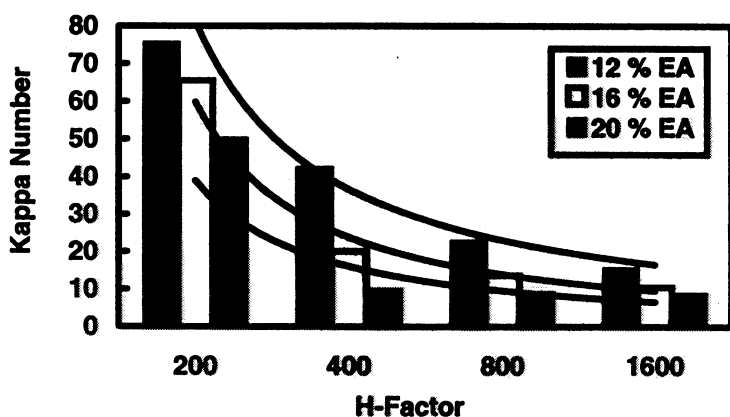


Figure 1: Effect of EA on H-Factor - Kappa Number Relationship in Kraft Cooking of Birch.

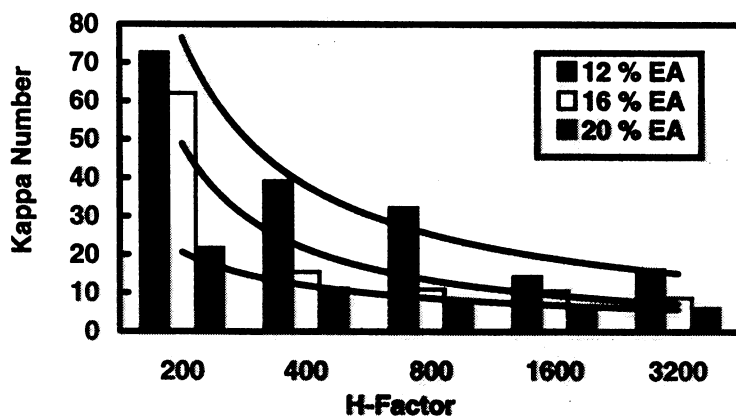


Figure 2: Effect of EA on H-Factor - Kappa Number Relationship in Kraft Cooking of Maple

Larger samples of both birch and maple pulps were then prepared with unbleached kappa numbers of ~20 at EA levels of 14 and 20%. Table 1 shows the unbleached properties of the pulps.

The results indicate that, in the case of birch, increasing EA gave an unbleached pulp of higher brightness, but lower yield, higher rejects and lower viscosity. However, for maple, pulping with high-EA produced pulp much higher in brightness than its low-EA counterpart, at comparable yield, rejects and viscosity levels. Increasing the digester alkalinity thus significantly reduces the cooking time with no significant effect on pulp yield and viscosity in the case of maple.

**Table 1: Unbleached Pulp Properties**

Hardwood species	Birch		Maple	
	EA, % (Na <sub>2</sub> O)	H-Factor	Kappa Number	Total Yield, %
EA, % (Na <sub>2</sub> O)	14	20	14	20
H-Factor	880	284	636	257
Kappa Number	19.4	18.7	20.4	20.3
Total Yield, %	51.9	50.5	51.3	51.9
Screened Yield, %	49.3	44.8	49.8	50.8
Brightness, % ISO	30.2	36.7	34.8	43.5
Viscosity, mPa.s	71.8	48.7	41.6	41.5
Black Liquor:				
pH	13.2	13.6	13.2	13.6
NaOH by titration to pH 11, g/l (Na <sub>2</sub> O)	5.5	7.9	4.5	23.9

Constant cooking conditions: Sulfidity, 25%; liquor to wood ratio, 4.0; maximum temperature 170°C.

The increase in birch rejects that accompanies increased EA is presumably a result of the associated reduction in H-factor, which decreases the time available for transport of chemicals to the chip centers. Another factor which may contribute to a deficiency in alkali at the chip center is a high rate of alkali consumption at the chip exterior, as suggested by the observation that when EA was increased in birch cooks, most of the added alkali was consumed. In the maple cooks, on the other hand, very little of the additional alkali was consumed and rejects remained low.

#### **Response in the D<sub>0</sub>(EO) Partial Sequence**

Table 2 includes the results of bleaching in the first two stages with a kappa factor of 0.2 in the D<sub>0</sub> stage.

Increasing EA had no effect on brightness gain over the D<sub>0</sub>(EO) partial sequence, which was higher for maple. Increasing EA substantially improved the extent of delignification and reduced specific chemical consumption in these stages for maple but had no effect in the case of birch.

**Table 2: Unbleached Properties and Bleachability of Birch and Maple Kraft Pulp**

Unbleached pulp				D <sub>0</sub> (EO)			D <sub>1</sub> stage		D <sub>2</sub> stage		
Hard-wood species	EA %, Na <sub>2</sub> O	Kappa No.	Bright-ness, ISO	Delta Kappa/TAC	Bright-ness, ISO	Bright-ness, Gain	Bright-ness, Ceiling $b_0+b_1$	Res-ponse Factor $b_2$	D <sub>1</sub> stage charge, % on o.d.p.	Bright-ness, Ceiling $b_0+b_1$	Res-ponse Factor $b_2$
Birch	14	19.5	30.2	3.8	58.9	28.7	82.9	6.5	0.4	88.8	3.8
									0.8	89.2	8.9
									1.2	89.7	17.5
Birch	20	18.7	36.7	3.8	65.3	28.6	87.4	5.8	0.4	90.1	6.1
									0.8	90.1	n.r.
									1.2	91.1	2.5
Maple	14	20.4	34.8	3.9	66.3	31.5	87.8	4.9	0.4	92.0	5.3
									0.8	92.5	9.8
									1.2	92.3	n.r.
Maple	20	20.3	43.5	4.3	74.9	31.4	92.9	5.0	0.4	93.1	n.r.
									0.8	93.9	5.9
									1.2	94.0	n.r.

n.r. – not reported; standard error greater than 50% of the estimated value.

#### Response in the D<sub>0</sub>(EO) D<sub>1</sub> Sequence

In the D<sub>1</sub> stage the pulps were bleached with 0.4, 0.8 and 1.2% ClO<sub>2</sub>. A D<sub>1</sub> brightness response curve was thus developed for each of the D<sub>0</sub> (EO) pulps at three levels of ClO<sub>2</sub> charge. The response was characterized, as described earlier (8), by fitting the data with the following equation:

$$y = b_0 + b_1 [1 - \exp(-b_2 x)]$$

where

y = brightness of the pulp after D stage

x = % chlorine dioxide consumed (o.d. pulp basis) in the D stage

$b_0$  = brightness of the entering pulp

$b_1$  = maximum brightness gain

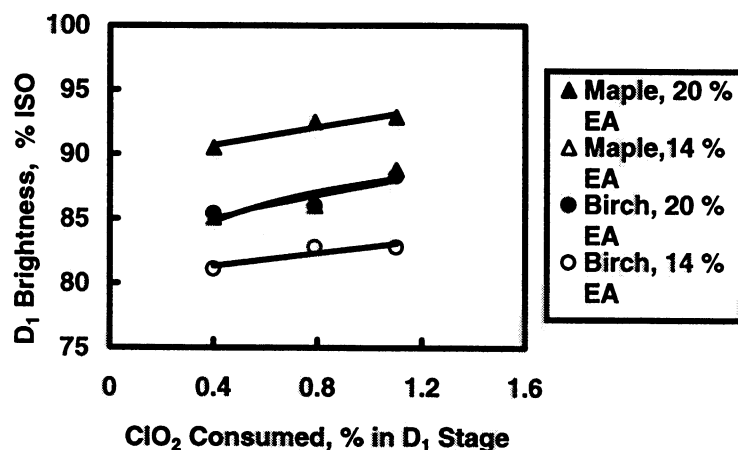
$b_2$  = brightness response factor

The sum, ( $b_0+b_1$ ) is the predicted brightness “ceiling,” the highest brightness that can be reached, regardless of how much ClO<sub>2</sub> is applied. The parameter  $b_2$  is a measure of the responsiveness of the brightness to increases in ClO<sub>2</sub> consumption at brightness levels below the ceiling.

The results are recorded in Table 2. The high-EA pulps were easily bleachable, as further illustrated in Figure 3. At any given ClO<sub>2</sub> charge in the D<sub>1</sub> stage, the brightness difference between low- and high-EA pulps was as much as 5 points. Most importantly, increasing EA resulted in very high brightness maple pulps having a ceiling of ~93% ISO. A practical implication of this is that increasing EA allows shortening of the bleaching sequence from 5 stages to 3 stages with associated benefits of energy and capital savings.

The D<sub>1</sub> stage model parameters shown in Table 2 reflect these observations. The predicted brightness ceilings are higher for maple than for birch and are increased by increasing EA. The response factor,  $b_2$ , is

unaffected by EA, suggesting that increasing EA has no effect on the ease of removal of the removable chromophores. The higher brightness ceiling of the high-EA pulps is apparently due to a reduction in the amount of intractable chromophores.



**Figure 3: Effect of EA Charge in Pulping on D<sub>1</sub> Stage Brightness**

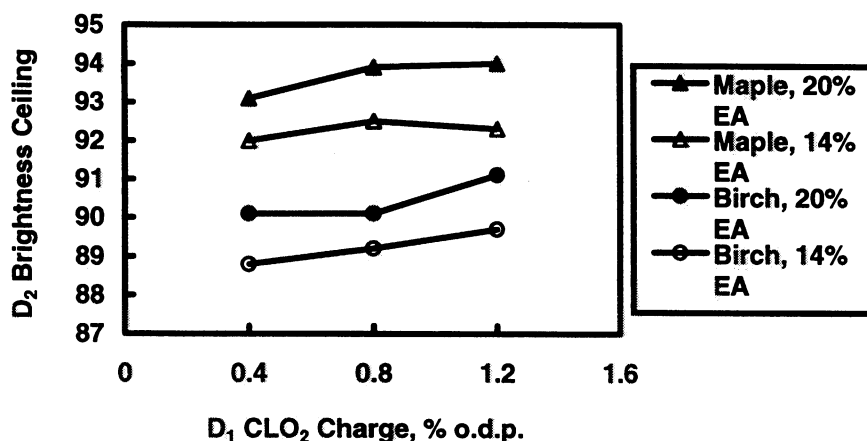
#### Response in the D<sub>0</sub>(EO)D<sub>1</sub>ED<sub>2</sub> Sequence

All of the D<sub>0</sub>(EO)D<sub>1</sub> pulps were further bleached by subjecting them to an alkaline extraction followed by a D<sub>2</sub> stage. In the final brightening stage, the pulps were bleached with three levels of ClO<sub>2</sub>, i.e., 0.2, 0.4 and 0.8%. Analysis of the D<sub>2</sub> response was done using the above model to arrive at brightness ceiling and brightness response factor values. The results are recorded in Table 2 and Figure 4.

For a given charge of ClO<sub>2</sub> in D<sub>1</sub>, the brightness ceiling was higher for high-EA pulps and higher for maple than for birch. For both species, the brightness ceiling was relatively insensitive to the D<sub>1</sub> stage ClO<sub>2</sub> charge, increasing slightly as the ClO<sub>2</sub> charge was increased from 0.4 to 1.2% in case the of birch.

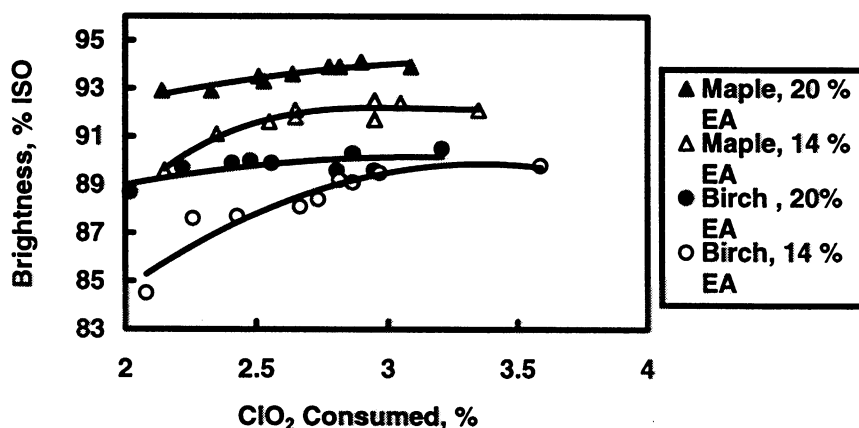
The response of the low-EA pulps to increasing D<sub>2</sub>-stage ClO<sub>2</sub> charge, as measured by  $b_2$ , was higher for pulps that had been bleached with higher levels of ClO<sub>2</sub> in the D<sub>1</sub> stage, indicating that the remaining chromophores had been in some way "preconditioned" by the additional D<sub>1</sub> stage ClO<sub>2</sub>. In the case of high-EA pulps, high levels of ClO<sub>2</sub> in the D<sub>1</sub> stage raised the brightness to such high levels, that the brightness entering the D<sub>2</sub> stage was already close to the ceiling. Consequently, the response in the D<sub>2</sub> stage was depressed, and  $b_2$  decreased.





**Figure 4: Effect of EA Charge on D<sub>2</sub> Brightness Ceiling for Various Charges of ClO<sub>2</sub> in D<sub>1</sub> Stage.**

Figure 5 shows the brightness after 5 stages of bleaching plotted as a function of total ClO<sub>2</sub> consumed. By increasing the digester alkalinity, bleaching response can be substantially improved. Both hardwood species exhibit better bleachability when cooked with high EA. They possess higher brightness ceilings and consume less bleaching chemical to achieve a given target brightness. Maple pulps give much higher brightness than birch at all levels of ClO<sub>2</sub> consumption.



**Figure 5: Effect of EA on ECF Bleaching [D<sub>0</sub>(EO)D<sub>1</sub>ED<sub>2</sub>] of Birch and Maple Kraft Pulp**

#### Effect of EA on Hexeneuronic Acid Content

The hexeneuronic acid (HexA) content of birch and maple pulps as a function of EA is recorded in Table 3. The presence of HexA in kraft pulps has been reported only recently due to their instability in conventional acid hydrolysis conditions. 4-O-Methyl-D-Glucuronic acid units which exist in xylan are in part converted to unsaturated hexeneuronic acid groups during kraft cooking (9). Because of their unsaturation, they react with bleaching chemicals, including ClO<sub>2</sub>, and contribute to kappa number of the pulp to a significant extent, especially in the case of hardwood pulps. In ECF bleaching, a part of the oxidizing power of ClO<sub>2</sub>

will be lost in this undesirable reaction, leaving less  $\text{ClO}_2$  for the reaction with the residual lignin in the pulp. Depending on the cooking conditions, the HexA content may differ profoundly and subsequently affect the bleachability of these pulps (10).

**Table 3: Effect of EA on Hexeneuronic Acid Content**

Hardwood species	Hexeneuronic acid, $\mu\text{M/g}$ pulp		
	Low-EA	High-EA	Change, %
Birch	56.7	51.9	8.5
Maple	59.4	51.0	14.1

The analysis of both birch and maple pulps showed that the alkalinity of the cooking liquor affected the amount of HexA. As the EA charge was increased from 14 to 20%, the HexA decreased by 8 and 14% for birch and maple, respectively. The better bleachability of high-EA pulps may be related to the lower HexA contents in these pulps as compared to their low-EA counterparts. In this regard, it is noteworthy that, when EA was increased,  $D_0(\text{EO})$  delignification was improved more in the case of maple than in that of birch, just as the HexA content was decreased more for maple.

## SUMMARY AND CONCLUSIONS

The results of these initial studies indicate that the alkalinity of the cooking liquor affects the nature and bleachability of the pulp produced. An important outcome of this work was that high-EA pulping emerged as an attractive option. High-EA pulping significantly reduces the cooking time and produces brighter pulps at comparable pulp yield and viscosity. It also greatly enhances maple pulp bleachability by allowing very high brightness pulps to be produced in only 3 stages of ECF bleaching. High-EA pulping of this species has the potential to increase digester throughput without any negative effect on pulp yield and viscosity and with improved bleachability. For birch, high EA has a negative effect on pulp yield and viscosity although it greatly improves the ECF bleaching response. Increasing the alkalinity of the cooking liquor decreased the hexeneuronic acid content, especially in the case of maple. Improved  $D_0(\text{EO})$  delignification of high-EA maple pulps may be related to their lower HexA contents.

## REFERENCES

1. U.S. Environmental Protection Agency, 40 CFR Part 430 "The Pulp, Paper and Paperboard Point Source Category," <http://www.epa.gov/OST/pulppaper/reg.html>, November 1997.
2. McDonough, T.J., Rawat, N., Turner, M., 51<sup>st</sup> Appita Annual General Conference, "ECF bleachability of softwood kraft pulps made with different effective alkali charges," Vol. 1, pp 255-260 (1997).
3. Laganier, M., Champagne, F., Graff, S., and Nadezhdin, A., Pulp & Paper Canada, "Accelerated batch cooking of hardwood," Vol. 98, pp 157-159 (1997).
4. Aurell, A., Svensk Papperstidning, "Kraft pulping of birch," Vol. 67, no. 2, pp 43-49 (1964).
5. Reeve, D.W., Weishar, K.M., Proceedings 1997 TAPPI Pulping Conference, TAPPI PRESS, Atlanta, pp 121-126.
6. Hanna, R.J., Fisher, J.J., Krohn, M.J., Goyal, G.C., Packwood, R.E., Ragauskas, A.J., Proceedings 1998 International Pulp Bleaching Conference, pp 323-328.
7. Vuorinen, T., Teleman, A., Fagerstrom, P., Buchert, J., Tenkanen, M., Proc. 1996 TAPPI International Pulp Bleaching Conference, pp 43-51
8. McDonough, T.J., Proceedings 1996 TAPPI Pulping Conference, TAPPI PRESS, Atlanta, page 201.
9. Teleman, A., Harjunpaa, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., and Vuorinen,.

- Carbohydrate Research, 272:55 (1995).
10. Buchert, J., Teleman, A., Harjunpaa, V., Tenkanen, M., Viikari, L., and Vuorinen, T., Tappi Journal, Vol. 87(11), pp 125 (1995).

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